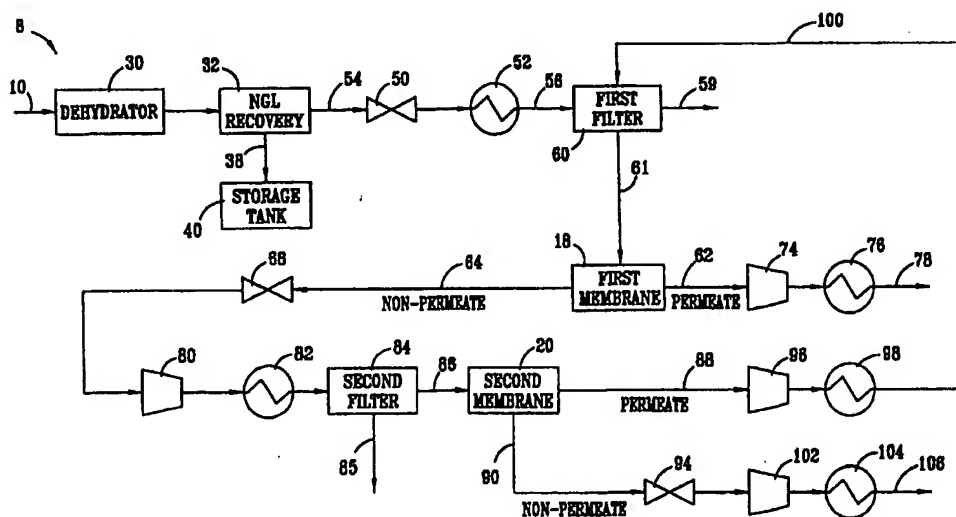




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(54) Title: PROCESS FOR SEPARATING NATURAL GAS AND CARBON DIOXIDE



(57) Abstract

A process for separating natural gas and carbon dioxide from a raw feed stream, such as in carbon dioxide for EOR processes. Separation is by membrane separation at low pressures. By utilizing low pressure separation, highly selective membranes can be used and recycling becomes practical.

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PROCESS FOR SEPARATING
NATURAL GAS AND CARBON DIOXIDE

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a process for separating natural gas and carbon dioxide from a raw feed stream. More particularly, the present invention relates to a process for recovering high purity carbon dioxide and methane from a raw feed stream where carbon dioxide is utilized in enhanced oil recovery.

BACKGROUND OF THE INVENTION

Natural gas streams containing carbon dioxide in high concentrations occur naturally and as the result of enhanced oil recovery (EOR) operations. During EOR operations, carbon dioxide is injected into mature oil fields to improve the miscibility of the oil and enhance its production to the surface. Gas returning to the surface, along with the oil, contains hydrocarbon gases and carbon dioxide. The carbon dioxide is separated from the hydrocarbon gases and reinjected. The hydrocarbon stream is further treated and either used for fuel gas or sold to a pipeline.

Heretofore, attempts to recover carbon dioxide from associated gases were by processes using a chemical solvent to scrub the gas and thereafter distilling to recover the carbon dioxide. Such methods were costly and met with problems regarding corrosion and solvent degradation. Examples of such processes and methods to alleviate the corrosion problems are found in U.S. Patent No. 2,065,112 which issued in 1936, U.S. Patent No. 2,399,142 which issued in 1946, U.S. patent No. 2,377,966 which issued in 1945, U.S. Patent No. 4,477,419 which issued in 1984, U.S. Patent No. 3,137,654 which issued in 1964. The alkanolamine process described in some of these patents is still widely used today.

More recently, commercial membrane technology has been developed for separating acid gases like carbon dioxide and hydrogen sulfide from light hydrocarbon gases. Examples of such art are found in U.S. Patent No. 4,130,403 which issued December 19, 1978 to T.E. Cooley et.al., U.S. Patent No. 4,639,257

5 which issued January 27, 1987 to Melvyn Duckett et.al., and U.S. Patent No. 5,233,837 which issued August 10, 1993 to Richard Callahan. The features of these patents, particularly the use of membrane separation, was a definite step forward in the carbon dioxide separation art. However, the prior art in this field continues to suffer from overall efficiency of the process and undesirable membrane life.

10 Furthermore, the prior art is not readily adapted to low feed stream pressures.

Accordingly, a continuing search has been directed to the development of a system and method which can separate carbon dioxide from natural gas, particularly in low pressure EOR processes.

SUMMARY OF THE INVENTION

15 The invention includes a process for separating carbon dioxide from a raw feed stream containing hydrocarbon gases and carbon dioxide. Compared to conventional processes, this process requires less power because the membrane operates at relatively low feed stream pressures. Relatively high purity carbon dioxide and a separated hydrocarbon gas are recovered.

20 In one aspect of the invention, a membrane having relatively high selectivities may be utilized to increase the purity of recovered gases.

In another aspect of the invention, the feed gas stream may be dehydrated, to protect the membrane, to increase the efficiency and effectiveness of gas separation, and to reduce power requirements.

25 In yet another aspect of the invention, liquid hydrocarbons are removed from the feed gas stream to protect the membrane, to increase the efficiency and effectiveness of the gas separation, and to reduce power requirements.

In still another aspect of the invention, turbo expansion of the feed stream gas is incorporated to recover power upstream of the first membrane.

30 In still another aspect of the invention, membranes are employed in a multi-stage configuration.

5 In yet another aspect of the invention, gas from one or more downstream membrane stages is recycled to one or more upstream stages, to heighten the purity of recovered gas and the system efficiency.

In still another aspect of the invention, a feed stream is passed into the bore of the membrane to separate a portion of one or more factions of the feed stream.

10 BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the invention and its advantages will be apparent from the detailed description taken in conjunction with the accompanying drawings in which:

FIGURE 1 is a diagrammatic view of a process embodying features of the present invention;

FIGURE 2 is a diagrammatic view of a first alternate embodiment of the process shown in FIG. 1 in which the feed stream pressure is relatively low; and

FIGURE 3 is a diagrammatic view of a second alternate embodiment of the process shown in FIG. 1, in which the feed stream pressure is relatively high.

20 DETAILED DESCRIPTION OF THE INVENTION

In the discussion of the FIGURES, the same reference numerals will be used throughout to refer to the same or similar components. In the interest of conciseness and clarity, various other components known to the art, such as wellheads, valves, instruments, and the like necessary for the operation of the process, have not been shown or discussed in detail.

25 In accordance with the present invention, a process is disclosed for separating carbon dioxide from a raw gas feed stream which contains natural gas and carbon dioxide and may contain other constituents such as water, nitrogen, oxygen, and hydrogen sulfide. Such a raw feed gas stream may come from any of a number of sources, but is often a by-product of enhanced oil recovery (EOR) operations. It should be understood that the pressures and volumes of by-product streams from EOR operations vary over time and from location to location. Therefore, the system described is sufficiently

5 flexible to be used with raw gas streams having optimum pressure, low pressure, or high pressure, as will be described below with respect to FIGURES 1, 2, and 3, respectively.

FIGURE 1 illustrates a process 8 for separating carbon dioxide from a raw gas feed stream at an optimum pressure for a first membrane 18 and a second membrane 20, such optimum pressure ranging from about 75 to about 150 psig and, typically, from about 90 to about 110 psig and, preferably, being about 90 psig. As discussed further below, the membranes 18 and 20 are preferably bore-fed, highly selective, hollow-fiber membranes operable at relatively low pressures, and are effective to increase the purity of recovered gases.

15 The raw feed gas stream at the optimum pressure enters a dehydration column 30 via a line 10. In the dehydration column 30, water in the raw feed gas stream is adsorbed on a desiccant (not shown) and the dry gas is delivered to a natural gas liquids (NGL) recovery unit 32. In the NGL recovery unit 32, the dehydrated feed gas stream is cooled to a temperature sufficient to condense a portion of the feed stream, primarily valuable heavier hydrocarbons which are then removed via a line 38 to a storage tank 40.

20 The resulting treated raw gas stream is then delivered downstream via a line 54 through a pressure control valve 50 and heat exchanger 52 and via a line 56 to a first filtering system 60. The pressure control valve 50 finely controls the pressure of the gas stream so that, just upstream of the first membrane 18, the pressure of the gas stream is in the range of from about 75 to about 150 psig and, typically, from about 90 to about 110 psig and, preferably, about 90 psig, for optimum separation. The heat exchanger 52 finely adjusts the temperature so that, just upstream of the first membrane 18, the temperature of the gas stream is in the range of from about 75°F to about 150°F and, typically, from about 75°F to about 120°F and, preferably, about 100°F, for optimum separation.

30 The temperature and pressure controlled feed stream in the line 56 and a recycle stream (described below) in a line 100 are passed through the first filtering system 60 where the streams are mixed and coalesced, thereafter absorption filtered and thereafter

5 particulate filtered to form a first stage membrane feed stream on a line 61, and a waste product on a line 59, which waste product is treated in any suitable manner well-known in the art. The first stage membrane feed stream enters the bore (not shown) of the first stage membrane 18, and is separated into a high purity first permeate stream 62 and a first nonpermeate stream 64. The bore side pressure within the membrane 18 is controlled by
10 a pressure control valve 68 to maintain the pressure of the non permeate stream 64 in a range of from about 5 to about 30 psig and, preferably, about 15 psig.

The high purity first permeate stream 62 passing from the first stage membrane 18 is compressed by a compressor 74 and cooled by a heat exchanger 76. The compressed and cooled first permeate stream 62 is then recovered via a line 78 and
15 transferred to a pipeline (not shown) for EOR, is liquified, or is employed in other suitable applications.

The temperature and pressure of the nonpermeate stream 64 discharged from the first stage membrane 18 are altered to correspond to optimum operating temperature and pressure ranges of the second stage membrane 20 by passing the stream 64 through a
20 compressor 80 and a heat exchanger 82. The altered stream then passes through a second filtering system 84. While not shown, within the second filtering system 84, the stream 64 passes through a coalescing filter, thereafter through an absorption filter, and thereafter through a particulate filter. The filtered, temperature and pressure altered nonpermeate stream is thereafter passed via a line 86 into the bore (not shown) of the
25 second stage membrane 20 wherein the nonpermeate stream is separated into a second, or recycle, permeate stream 88 and a second nonpermeate stream 90. The pressure of the stream 90 is controlled by a pressure control valve 94. The filter 84 also generates a waste product onto a line 85 which waste product is treated in any suitable manner well-known in the art.

30 A compressor 96 and heat exchanger 98 thereafter alter the pressure and temperature of the second permeate stream 88 to preselected pressure and temperature ranges corresponding to optimum operating ranges of the first membrane 18. The altered

5 second permeate stream 88 is then passed via the line 100 back to the first filtering system 60 for additional recycling through the membranes 18 and 20.

The nonpermeate stream 90 passing from the second stage membrane 20 is compressed by a compressor 102 and cooled by a heat exchanger 104. The compressed- and cooled nonpermeate stream 90 is recovered via a line 106 and transferred to a pipeline, used as fuel, or employed in other suitable applications.

10 FIGURES 2 and 3 depict alternate embodiments of the process 8 shown in FIG. 1. Since the embodiments depicted in FIGS. 2 and 3 contain many components that are identical to those of the previous embodiment, these components are referred to by the same reference numerals and will not be described in any further detail.

15 According to the embodiment shown in FIGURE 2, the process 8 is adapted to receive a relatively low pressure raw feed gas stream on the line 10. To this end, prior to entering the dehydrator 30, the feed stream passes through and is compressed by a compressor 26 by which the pressure is increased to the optimum pressure for the membranes 18 and 20. The compressed stream is then passed through a heat exchanger 20 28 by which the compressed feed stream is cooled and thereafter delivered to the dehydration column 30. The embodiment of FIG. 2 is otherwise identical to that of FIG. 1.

25 According to the embodiment shown in FIGURE 3, the raw feed gas stream enters the process 8 via the line 10 at a pressure higher than the optimum pressure for the membranes 18 and 20 and is passed through the dehydration column 30 and NGL recovery unit 32 as described above. The pressure of the treated gas stream is then let down to the optimum pressure for membranes 18 and 20 through a series of expansion valves or turbo expanders, such as two turbo expanders 46 and 47. The refrigeration created by the expansion of the gas is recovered in exchangers 48 and 49 and 30 subsequently used in the natural gas liquids recovery unit to reduce the input refrigeration requirement and thus improve the efficiency of the overall process. More or less than two turbo expanders 46 and 47 and heat exchangers 48 and 49 may be used to reduce the

5 pressure and recover the refrigeration created. The embodiment of FIG. 2 is otherwise identical to that of FIG. 1.

The process of this invention is designed for raw feed streams which have a carbon dioxide content in the range of about 10 to about 90 percent by volume. The pressure of the first and second membrane feed streams is maintained in the range of
10 about 80 psig. to about 100 psig., preferably at about 90 psig. for optimum operating conditions. The temperature of the first and second membrane feed streams is maintained in the range of about 90 to about 110 degrees F., preferably at about 100 degrees F. for optimum operating conditions. The incoming membrane feed streams enter the bore of the membrane and are separated by the membrane.

15 The membranes can be formed of polysulfone, polyimide, polyamide, glassy polymer or cellulose acetate. In the preferred embodiment, preferably both membranes 18 and 20 comprise the same material, and preferably both have a selectivity greater than about 15:1 of carbon dioxide to hydrocarbons in the range of C1 to C6. The differential pressure of the nonpermeate stream of both membranes 18 and 20 is typically maintained
20 in the range of about 5 to about 30 psig, and preferably at about 15 psig.

The permeate stream 62 from the first stage membrane 18 is preferably maintained to contain carbon dioxide in an amount substantially equivalent to or greater than about 60% carbon dioxide by volume, and is passed to a pipeline, liquified, or is used directly.

The nonpermeate stream 90 from the second stage membrane 20 is preferably
25 maintained to contain carbon dioxide in an amount less than about 20% carbon dioxide by volume. The nonpermeate stream 90 flows to a pipeline or to downstream processing.

In the dehydration column 30, substantially all of the water vapor contained in the raw feed gas is removed to protect the membrane, to increase the efficiency and effectiveness of gas separation, and to reduce power requirements. The dehydration
30 process can be recirculated triethylene glycol where the raw feed gas passes up through the column 30 in countercurrent flow to a lean triethylene glycol solution; adsorption by

5 a desiccant where the raw feed gas passes down through a bed containing molecular sieves or activated alumina; or other combinations of these two dehydration processes.

In the NGL recovery column 32, portions of the raw feed stream are liquefied to remove from the system hydrocarbon portions having a carbon content predominantly heavier than C3 (propane). These removed portions are passed to the storage tank 40
10 since they are valuable products and include such heavier hydrocarbons.

The raw feed stream can be cooled to remove the heavier hydrocarbons by evaporating liquid refrigerant and bringing the resultant gaseous refrigerant into indirect heat exchange relationship with the raw feed stream in the column 32. It should also be understood that the raw feed stream can be cooled in column 32 by indirect heat
15 exchange with an expanded portion of the raw feed stream.

In order to improve efficiency of the process and avoid the waste of power and cooling and heating properties of the process, generated physical properties of the system are utilized.

Referring to FIG. 2, the compression of gasses in the process produces heat which
20 can be efficiently utilized in heat exchange relationship with other portions of the feed stream.

Referring to FIG. 3, turbine expanders 46,47 can be directly connected to drive a compressor of the process (not shown) or connected to a generator for the recovery of electrical power. The expansion of gases in the process generates cooling and this
25 cooling can be efficiently utilized in heat exchange relationship with other portions of the feed streams.

In addition to the membrane gas - separation configuration shown in Fig. 1, the present invention can employ the configuration and system disclosed in co-pending U.S. Patent Application Serial No. 09/057,126, filed April 8, 1998, entitled MEMBRANE
30 PROCESS FOR PRODUCING CARBON DIOXIDE, to Paul A. Daus, et al., which is hereby expressly incorporated by reference.

EXAMPLE I

5 With reference to FIGURE 1, a raw gas of 31.054 MMSCFD at 85°F and 155 psig, as described in Table 1, enters the process 8 on the line 10. There is sufficient pressure to move the gas through the process, so the raw gas first enters the dehydration unit 30. Within the dehydration unit 30, the raw gas is dehydrated by a desiccant filter
10 that requires 1,117 SCFH of fuel gas to remove 135.145 lbs/hr of water.

The dry raw gas containing carbon dioxide, heavy hydrocarbons, and hydrogen sulfide, as described in Table 1, enters the Natural Gas Liquid recovery unit 32 where 41.439 gpm of liquid hydrocarbons are removed by a commercial propane refrigeration plant. The liquid hydrocarbon product stream is further described in Table 1. The
15 refrigeration plant requires a total of 901.2 brake horsepower and 738 gpm of cooling water.

The raw gas stream leaves the propane refrigeration plant without sufficient pressure to economically justify turbine expansion for power recovery, so it enters the membrane separation portion of the process. It is separated into 20.703 MMSCFD of a
20 permeate stream containing 94.029% carbon dioxide by volume and 8.566 MMSCFD of a nonpermeate stream containing 2.704% carbon dioxide by volume as further described in Table 1. The membrane separation portion of the process requires a total of 778.8 brake horsepower and 139 gpm of cooling water.

The permeate carbon dioxide product stream leaves the membrane portion of the
25 process on the line 62 at 85°F and 0 psig and enters the compressor 74 where the gas is compressed to meet downstream specifications. The non-permeate hydrocarbon product stream leaves the membrane portion of the process at 96°F and 80 psig and enters the compressor 102 where the gas is delivered downstream to be used as fuel gas or sold to a pipeline.

30 A total of 1.129 short tons per day of carbon dioxide on a 100% basis is produced by the process and requires a total of 1.680 brake horsepower, 877 gpm of cooling water.

5 1,117 SCFH of fuel gas, and 520 Generon membrane modules, as summarized in Table
3.

EXAMPLE II

Five million standard cubic feed per day of raw feed gas at 60°F and 800 psig as
further described in Table 2 enters the dehydration unit 30 and 1.457 lbs/hr of water are
10 removed by a desiccant media. The dehydrated raw gas pressure is then let down by an
expansion valve to 285.3 psig, resulting in a temperature drop to -10°F. The raw feed
gas then enters a heat exchanger where it is heated back to 70°F producing 429,500
BTU/hr of cooling. The dehydrated raw gas pressure is further let down by a second
expansion valve to 102 psig, resulting in a temperature drop to 50.3°F. The raw feed gas
15 then enters a second heat exchanger where it is heated back to 70°F producing 97,450
BTU/hr of cooling. The cooling available is used to precool product CO₂ gas prior to
liquefaction in the downstream food grade liquid CO₂ plant.

The 5 MMSCFD of dehydrated and pressure adjusted raw feed gas then enters a
filter 60 where it is mixed with 1.279 MMSCFD of permeate at 100°F that has been
20 recycled from the second stage membrane 20 making a combined stream of 6.279
MMSCFD of feed gas at 91.7°F. The combined gas stream then passes through a
coalescing filter, adsorption filter, and particulate filter within the filter 60 before
entering the bore side of the first stage membrane 18 consisting of 69 membrane modules
where separation takes place. In the first stage membrane 18, 83.42% of the incoming
25 CO₂ and 3.33% of each hydrocarbon component and nitrogen permeates the membrane
and exits at 0 psig generating a CO₂ vapor product stream of 3.858 MMSCFD
containing 98.5% CO₂ by volume. In this example the CO₂ vapor stream is then sent
to a commercial food grade liquid CO₂ production plan to produce 208 short tons pers
day of liquid CO₂ product at -15°F and 250 psig.

30 A quantity of 2.421 MMSCFD of nonpermeate product stream from the first stage
membrane, having a temperature of 90.7°F and a pressure of 75 psig, then enters the
second stage membrane 20 consisting of 94 membrane modules. No recompression of

the nonpermeate stream is required in this case. In the second stage membrane, 95.85% of the incoming CO₂ and 33.34% of each hydrocarbon component and nitrogen permeates the membrane and exists at 0 psig. The permeate stream is next recompressed to 102 psig then cooled to 100°F requiring 217.4 brake horsepower before being recycled to the inlet of the filter system 60 and mixed with the raw feed gas stream ahead of the first stage membrane 18. A quantity of 1.142 MMSCFD of nonpermeate product stream from the second state membrane, containing 89.5% hydrocarbon, 2.7% CO₂, and 7.8% nitrogen at a temperature of 90.4°F and a pressure of 70 psig, then enters a product compressor where the pressure is increased to 202 psig requiring 68.5 brake horsepower and then a heat exchange where the product gas is cooled to 100°F.

The process gas rates and utility requirements for each example are summarized in Table 3.

TABLE 1
(Example 1)

Stream	Raw Gas	NGL	CO ₂	HC	
Rate (MMSCFD)	31.054			20.703	856
Rate (GPM @ T/P)		41.439			
Temperature (DEG. F.)	85.000		150.13	85.011	
				96.339	
Pressure (PSIG.)	155.000	154.000	0	80.000	
Composition (by volume)					
Methane	19.228%	0.000%	3.669%	60.839%	
Ethane	6.119%	0.008%	1.168%	19.361%	
Propane	5.529%	38.262%	0.652%	10.804%	
I-Butane	0.640%	8.560%	0.032%	0.528%	
N-Butane	1.930%	28.108%	0.072%	1.190%	
I-Pentane	0.430%	7.295%	0.005%	0.085%	
N-Pentane	0.490%	8.424%	0.005%	0.077%	

5	N-Hexane	0.420%	7.532%	0.001%	0.012%
	N-Octane	0.100%	1.809%	0.000%	0.000%
	Nitrogen	1.390%	0.000%	0.265%	4.398%
	Carbon Dioxide	63.434%	0.000%	94.029%	2.704%
	Hydrogen Sulfide	0.070%	0.003%	0.103%	0.003%
10	Water	0.220%	0.000%	0.000%	0.000%

TABLE 2
(Example 2)

5	Stream	Raw Gas	CO ₂	HC
	Rate (MMSCFD)	5.000	3.856	1.140
	Temperature (DEG. F.)	60.000	81.345	
10	100.000			
	Pressure (PSIG)	800.000	0	200.000
	Composition (by volume)			
	Methane	21.294%	1.356%	88.745%
	Ethane	0.170%	0.011%	0.709%
15	Propane	0.000%	0.000%	0.000%
	I-Butane	0.000%	0.000%	0.000%
	N-Butane	0.000%	0.000%	0.000%
	I-Penane	0.000%	0.000%	0.000%
	N-Pentane	0.000%	0.000%	0.000%
20	N-Hexane	0.000%	0.000%	0.000%
	N-Octane	0.000%	0.000%	0.000%
	Nitrogen	1.871%	0.119%	7.798%
	Carbon Dioxide	76.650%	98.514%	2.748%
	Hydrogen Sulfide	0.000%	0.000%	0.000%
25	Water	0.015%	0.000%	0.000%

TABLE 3

5	Feed Rate and Conditions	Example 1	Example 2
	Inlet gas rate (MMSCFD)	31.054	5.000
	CO ₂ feed concentration (MOLE%)	63.44%	76.65%
	Inlet gas temperature (DEG. F.)	85	60
10	Inlet gas pressure (psig)	155	800
	Product Rates and Conditions		
	Water Removed (lbs/hr)	135.145	1.457
	Liquid HCS Removed (USGPM@T/P)	41.439	
15	CO ₂ Produced (MMSCFD)	20.703	3.856
	CO ₂ Produced on 100% basis (T/day)	1,129	216.3
	HC Produced (MMSCFD)	8.566	1.141
	Utilities		
20	Fuel gas (dryer) (SCFH)	1,117	25
	Booster Refrigerant		
	Compressor (BHP)	424.5	
	High Stage Refrigerant		
	Compressor (BHP)	476.7	
25	Recycle Membrane		
	Compressor (BHP)	778.8	217.4
	Cooling water @ 15F Rise (USGPM)	877	58
	Refrigeration made available		
	@ -10F. (BTU/Hr)		429.500
30	Refrigeration made available		
	@ -50F. (BTU/Hr)		97.450

5 **Summary**

Net compressor BHP required

(BHP)	1,680	217*
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Cooling water required (USGPM)	877	58
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Fuel gas required (SCFH)	1,117	25
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10 Refrigeration available (tons)		44
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Membrane modules required	520	163
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*Does not include HC product compressor.

15 The purity of the permeate carbon dioxide product stream 62 from the first stage membrane 18 and the purity of the nonpermeate hydrocarbon product stream 90 from the second stage membrane 20 are greatly increased by the novel techniques employed in the process, specifically the use of bore fed, highly selective membranes operating at low pressure where the permeate gas stream from the second stage membrane 20 is recycled to the first stage membrane 18. The novel approach of using low pressure permits the use of a highly selective membrane and makes recycle practical.

20 Removal of contaminants, such as water, heavier hydrocarbons, compressor oil, and particulate, ahead of the membranes by the first and second filtering systems 60 and 84 extends the life of the membranes.

25 When a high pressure raw gas stream enters the process 8 on the line 10, as shown in FIGURE 3, then the overall external power required by the process is further reduced because, as the gas stream flows through the turbine expanders 46 and 47 and expands, both mechanical horsepower and the cooling are produced and recovered for use by the process. The mechanical power recovered is used to make electric power either with a generator or by directly coupling shafts of the turbine expanders 46 and 30 47 to compressor shafts. The cooling that results from expanding the raw gas is used to reduce the external cooling required by the process to achieve the optimum

5 membrane performance and may also be used to reduce the external refrigeration needed in the natural gas liquid recovery plant 32.

Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions, and alterations can be made therein without departing from the spirit and scope of the invention as defined by the
10 appended claims. For example, where the raw feed gas contains hydrogen sulfide in amounts less than about 5%, the hydrogen sulfide can either be removed before dehydration or it will permeate along with the carbon dioxide and can be removed from the product gas streams by downstream treating processes. Other aspects, objects and advantages of this invention can be obtained from a study of the drawings, the
15 disclosure, and the appended claims.

5 WHAT IS CLAIMED IS:

1. A process for separating carbon dioxide from a raw feed stream containing natural gas and carbon dioxide, comprising:

dehydrating the raw feed stream;

10 liquefying and removing from the system, natural gas liquids from the raw feed stream and resultingly forming a treated feed stream:

altering the temperature and pressure of said feed stream to preselected values of an optimum operating range of a first stage membrane and resultingly forming an altered feed stream;

15 filtering the altered feed stream in a first filtering system and forming a first stage membrane feed stream;

passing the first stage membrane feed stream through the first stage membrane and resultingly separating said feed stream into a first permeate stream and a second nonpermeate stream;

recovering the first permeate stream;

20 altering the temperature and pressure of the first nonpermeate stream to preselected values of a second stage membrane and forming an altered recyclable feed stream;

filtering the altered recyclable feed stream;

25 passing the recyclable feed stream through a second stage membrane and resultingly separating said recyclable feed stream into a second permeate stream and a second nonpermeate stream;

recovering the second nonpermeate stream;

altering the temperature and pressure of the second permeate stream to a preselected value of the optimum operating ranges of the first stage membrane; and

30 recycling the temperature and pressure altered second permeate stream into the first filter system.

5 2. The process, as set forth in claim 1, wherein the raw feed stream comprises hydrocarbons, nitrogen, oxygen, hydrogen, and carbon dioxide.

 3. The process, as set forth in claim 1, wherein the raw feed stream contains carbon dioxide in the range from about 10 to about 90 percent by volume.

10 4. The process, as set forth in claim 1, wherein the raw feed stream contains hydrogen sulfide.

 5. The process, as set forth in claim 1, wherein the raw feed stream contains
15 water vapor.

 6. The process, as set forth in claim 1, wherein the raw feed stream contains natural gas liquids.

20 7. The process, as set forth in claim 1, wherein the pressure of the first membrane feed stream is about 90 psig.

 8. The process, as set forth in claim 1, wherein the raw feed stream is dehydrated.

25 9. The process, as set forth in claim 8, wherein dehydration of the raw feed stream is in response to directly contacting the raw feed stream with an ethylene glycol solution.

30 10. The process, as set forth in claim 8, wherein dehydration of the raw feed stream is in response to directly contacting the raw feed stream with a desiccant.

5 11. The process, as set forth in claim 1, including cooling the raw feed stream, liquefying a portion of the raw feed stream, and removing the liquefied portion.

 12. The process, as set forth in claim 11, wherein the liquefied and removed portions of the raw feed stream includes heavier hydrocarbons.

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 13. The process, as set forth in claim 12, wherein the heavier hydrocarbons have a carbon content predominantly greater than about C3.

 14. The process, as set forth in claim 11, including evaporating liquid
15 refrigerant in indirect heat exchange relationship with the raw feed stream for cooling the raw feed stream to a temperature sufficient for liquefying a portion of said stream.

 15. The process, as set forth in claim 11, wherein the raw feed stream is cooled in response to indirect heat exchange with an expanded portion of the raw feed
20 stream.

 16. The process, as set forth in claim 1, wherein the feed stream is said high pressure feed stream and wherein the temperature and pressure are altered in response to expanding said high pressure feed stream through at least one expansion turbine.

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 17. The process, as set forth in claim 16, including altering the temperature and pressure in response to expanding said high pressure feed stream through a plurality of expansion turbines.

30 18. The process, as set forth in claim 16, including recovering power generated by expanding said high pressure feed stream through the expansion turbine.

5 19. The process, as set forth in claim 16, including recovering the cooling properties resulting from expansion of gases in the process and utilizing said cooling properties in heat exchange relationship within the process.

10 20. The process, as set forth in claim 1, wherein the altered feed stream is filtered by passing said stream, in the first filtering system, through an absorption filter, thereafter through a coalescing filter and thereafter through a particulate filter.

15 21. The process, as set forth in claim 20, including removing oil and particulate from the altered feed stream in response to passing said stream through the first filtering system.

20 22. The process, as set forth in claim 20, wherein the first nonpermeate feed stream is filtered by passing said stream, in the second filtering system, through an absorption filter, thereafter through a coalescing filter, and thereafter through a particulate filter.

25 23. The process, as set forth in claim 1, wherein the first stage membrane includes a membrane having a bore surface and a shell surface and including maintaining the pressure and temperature on the bore surface at a pressure in the range of about 80 to about 100 psig and at a temperature in the range of about 90°F degrees to about 110° F.

30 24. The process, as set forth in claim 23, wherein the pressure is maintained at about 90 psig, and the temperature is maintained at about 100 degrees F.

5 25. The process, as set forth in claim 1, wherein the first stage membrane has
a membrane formed of polysulfone, polyimide, polyamide, glassy polymer and cellulose
acetate.

10 26. The process, as set forth in claim 25, wherein the second stage membrane
has a membrane formed of one of polysulfone, polyimide, polyamide, glassy polymer,
and cellulose acetate.

15 27. The process, as set forth in claim 1, wherein the second stage membrane
has a membrane formed of one of polysulfone, polyimide, polyamide, glassy polymer,
and cellulose acetate.

20 28. The process, as set forth in claim 1, wherein the first stage membrane has
a membrane having a selectivity greater than 15:1 of carbon dioxide to hydrocarbons
in the range of C1 to C6.

25 29. The process, as set forth in claim 1, wherein the differential pressure of
the nonpermeate stream of the first stage membrane is maintained in the range of about
5 to about 30 psig.

30 30. The process, as set forth in claim 1, wherein the differential pressure of
the nonpermeate stream of the first membrane is maintained at about 15 psig.

30 31. The process, as set forth in claim 1, wherein the first stage membrane is
a hollow fiber membrane having a bore and wherein the altered feed stream is passed
into the bore of the membrane.

5 32. The process, as set forth in claim 31, wherein the second stage membrane is a hollow fiber membrane having a bore and wherein the first nonpermeate feed stream from the first stage membrane is passed into the bore of the membrane of the second stage membrane.

10 33. The process, as set forth in claim 1, wherein the second stage membrane is hollow fiber membrane having a bore and wherein the first nonpermeate feed stream from the first stage membrane is passed into the bore of the membrane of the second stage membrane.

15 34. The process, as set forth in claim 1, including compressing and cooling the nonpermeate stream from the first stage membrane prior to entry into the second stage membrane.

20 35. The process, as set forth in claim 34, wherein the non permeate stream from the first stage membrane is compressed by passing the nonpermeate stream through one of a reciprocating compressor, a centrifugal compressor, and a screw compressor.

25 36. The process, as set forth in claim 34, wherein the non permeate stream from the first stage compressor is compressed by passing the nonpermeate stream through a screw compressor.

30 37. The process, as set forth in claim 1, wherein the second stage membrane has a membrane having a selectivity of about 15:1 carbon dioxide to hydrocarbons in the range of C1 to C6.

5 38. The process, as set forth in claim 37, wherein the first stage membrane has a membrane having a selectivity of about 15:1 carbon dioxide to hydrocarbons in the range of C1 to C6.

10 39. The process, as set forth in claim 1, wherein the differential pressure of the second stage membrane is maintained in the range of about 5 to about 30 psig.

 40. The process, as set forth in claim 39, wherein the differential pressure of the nonpermeate stream from the second stage membrane is maintained at about 15 psig.

15 41. The process, as set forth in claim 39, wherein the differential pressure of the first stage membrane is maintained in the range of about 5 to about 30 psig.

20 42. The process, as set forth in claim 39, wherein the differential pressure of the non permeate stream of the first membrane is maintained at about 15 psig.

 43. The process, as set forth in claim 1, including compressing and cooling the permeate stream from the second stage membrane prior to recycling to the first membrane.

25 44. The process, as set forth in claim 43, wherein the permeate stream of the second stage membrane is compressed by passing said permeate stream through one of a reciprocating compressor, a centrifugal compressor, and a screw compressor.

30 45. The process, as set forth in claim 43, wherein the permeate stream of the second stage membrane is compressed by passing said permeate stream through a screw compressor.

5 46. The process, as set forth in claim 1, including maintaining the permeate stream from the first stage membrane to contain carbon dioxide in an amount substantially equivalent to or greater than about 60% carbon dioxide by volume.

 47. The process, as set forth in claim 1, including liquefying the first permeate
10 stream.

 48. The process, as set forth in claim 1, maintaining the nonpermeate stream from the second stage membrane at less than about 20% carbon dioxide by volume.

15 49. The process, as set forth in claim 1, wherein altering the temperature of at least a portion of the streams of the separating process, for cooling said streams, is in response to bringing the stream to be cooled into heat exchange relationship with a colder fluid resulting from expansion of a feed stream of the separating process.

20 50. The process, as set forth in claim 1, wherein altering the temperature of at least a portion of the streams of the separating process, for heating said streams, is in response to bringing the stream to be heated into heat exchange relationship with a hotter fluid resulting from compression of a feed stream of the separating process.

25 51. The process, as set forth in claim 1 including compressing a low pressure feed stream with a compressor to the optimum pressure.

 52. A process for separating carbon dioxide from a raw feed stream containing natural gas and carbon dioxide, said feed stream having one of a low, near
30 optimum and high pressure, comprising:

 dehydrating the raw feed stream:

5 condensing and removing natural gas liquid from the raw feed stream and forming a treated feed stream;

 coalescing, absorbing and particulate filtering the resultant altered, treated feed stream in a first filtering system and forming a first stage feed stream;

 passing the filtered feed stream from the first filtering system through a first
10 stage membrane, separating said feed stream into a first permeate stream and a second nonpermeate stream, and controlling the pressure of said non permeate stream in the range of about 5 to about 30 psig.;

 recovering the first permeate stream discharging from the first stage membrane;

 altering the temperature and pressure of the first nonpermeate stream to
15 preselected values of the optimum operating ranges of a second stage membrane:

 coalescing, absorbing and particulate filtering the resultant temperature and pressure altered first nonpermeate stream and forming a second stage feed stream;

 passing the second stage feed stream through a second stage membrane, separating said feed stream into a second permeate stream and a second nonpermeate
20 stream and controlling the pressure of said second nonpermeate stream in the range of about 5 to about 30 psig.;

 altering the temperature and pressure of the second permeate stream to preselected values of the optimum operating ranges of the first stage membrane; and

 recycling the temperature and pressure altered second permeate stream into the
25 first filtering system.

53. A process for separating carbon dioxide from a raw gas feed stream containing natural gas and carbon dioxide, comprising:

 providing first and second stage membrane, each membrane having an optimum
30 operating pressure and temperature range:

 increasing the pressure of the incoming raw gas feed stream to the optimum operating pressure range of the first stage membrane:

5 dehydrating the incoming raw gas feed stream and removing water from said stream;

 cooling the dehydrated feed stream to a temperature sufficient to condense a portion of said feed stream and removing natural gas liquid from the dehydrated feed stream and forming a resultant treated gas stream:

10 passing the resultant near optimum pressure treated gas stream through an associated heat exchanger, resultingly altering the temperature to a preselected operating temperature of the first stage membrane, and forming a resultant fourth stream;

 passing the resultant streams and a recycle stream through a first coalescing, 15 absorption and particulate filtering system and forming a first stage membrane feed stream;

 passing the filtered first stage membrane feed stream through the first stage membrane and separating therein said filtered feed stream into a first permeate stream and a first nonpermeate stream;

20 controlling the pressure of the non-permeate stream of the first stage membrane; recovering high purity permeate stream passing from the first stage membrane; altering the temperature and pressure of the nonpermeate stream passing from the first stage membrane to preselected temperature and pressure corresponding to optimum operating temperature and pressure of the second stage membrane;

25 filtering the nonpermeate stream through a coalescing, absorption, and particulate filter;

 passing the filtered, temperature and pressure altered nonpermeate stream through the second stage membrane and separating said nonpermeate stream into a recycle permeate stream and a non permeate stream:

30 controlling the pressure of the non-permeate stream exiting the second stage membrane:

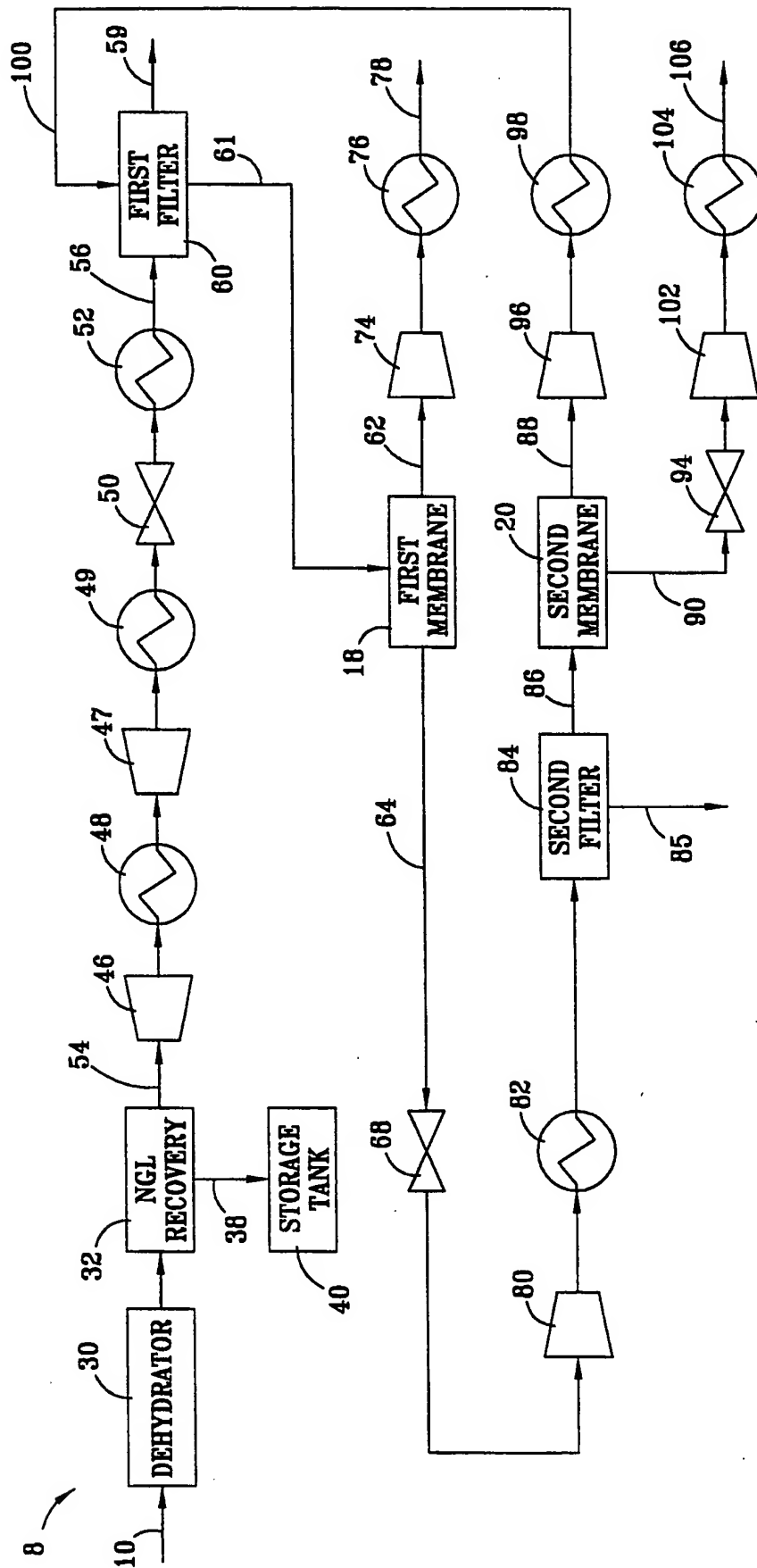
5 altering the temperature and pressure of the permeate stream passing from the second stage membrane to preselected temperature and pressure corresponding to optimum operating ranges of the first membrane. and recycling said permeate stream to the first filtering system; and

 recovering the nonpermeate stream passing from the second stage membrane.

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3/3

FIG. 3



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/20857

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/22 C10L3/10 C07C7/144

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D C10L C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 110 858 A (MONSANTO CO) 13 June 1984 (1984-06-13)</p> <p>page 1, line 3 - line 13 page 5, line 15 -page 6, line 32 page 8, line 7 - line 20 page 8, line 25 -page 10, line 23 page 12, line 31 -page 16, line 18; figures 1,3; table II</p> <p>--- -/--</p>	<p>1-4, 28, 34-38, 46, 48, 51-53</p>



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/20857

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 881 953 A (PRASAD RAVI ET AL) 21 November 1989 (1989-11-21)</p> <p>column 1, line 32 - line 52 column 3, line 24 -column 5, line 14 column 7, line 1 - line 59; claims 1-32; figure</p> <p>---</p>	<p>1,2,5,8, 10-14, 20,21, 25-28, 31-33, 51-53</p>
A	<p>GB 2 005 152 A (RAVIER P M H) 19 April 1979 (1979-04-19) page 3, line 119 -page 4, line 51; claims 1-10; figure 1</p> <p>---</p>	<p>1,34,43, 51</p>
A	<p>US 4 435 191 A (GRAHAM TOMMY E) 6 March 1984 (1984-03-06) claim 1; figures 1,4</p> <p>---</p>	<p>1</p>
A	<p>US 5 233 837 A (CALLAHAN RICHARD A) 10 August 1993 (1993-08-10) cited in the application the whole document</p> <p>-----</p>	<p>1-53</p>

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/20857

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0110858	A	13-06-1984	AU 2009083 A	19-04-1984
			JP 59130520 A	27-07-1984
			NO 833716 A	16-04-1984
US 4881953	A	21-11-1989	AT 110980 T	15-09-1994
			CN 1041113 A,B	11-04-1990
			DE 68918031 D	13-10-1994
			EP 0358915 A	21-03-1990
			ES 2059655 T	16-11-1994
			JP 2061815 C	10-06-1996
			JP 2157013 A	15-06-1990
			JP 5058767 B	27-08-1993
			KR 9312045 B	23-12-1993
			MX 166133 B	22-12-1992
GB 2005152	A	19-04-1979	FR 2403819 A	20-04-1979
			DE 2841760 A	05-04-1979
US 4435191	A	06-03-1984	AT 26410 T	15-04-1987
			CA 1219812 A	31-03-1987
			EP 0133174 A	13-02-1985
			JP 60068032 A	18-04-1985
			NO 842644 A	02-01-1985
US 5233837	A	10-08-1993	AT 158857 T	15-10-1997
			DE 69314346 D	06-11-1997
			DE 69314346 T	30-04-1998
			DK 658245 T	11-05-1998
			EP 0658245 A	21-06-1995
			ES 2110113 T	01-02-1998
			GR 3025783 T	31-03-1998
			JP 8501142 T	06-02-1996
			WO 9405960 A	17-03-1994

1/3

FIG. 1

